



METHOD OF MANUFACTURING A FERROELECTRIC SUBSTANCE  
THIN FILM AND FERROELECTRIC MEMORY USING  
THE FERROELECTRIC SUBSTANCE THIN FILM

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Background of the Invention

The present invention relates to a method of manufacturing a ferroelectric substance thin film and a method of manufacturing a ferroelectric memory, particularly to improvement of improve the crystallinity of the ferroelectric substance thin film.

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The ferroelectric memory being researched now is divided into two main areas. One is directed to a system for detecting reverse charge quantity of a ferroelectric capacitor constructed with the ferroelectric capacitor and a selective transistor.

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Another one is directed to a memory of a system for detecting a change of resistance of a semiconductor caused by a spontaneous polarization of the ferroelectric substance. The A typical one example of the this type of system is a MFSFET. This is an MIS structure using the ferroelectric substance for 20 a gate insulating film.

In any structure, it is known that film quality of the ferroelectric substance affects [[to]] the characteristics of memory significantly largely.

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Then, various methods for improving the crystallinity of the ferroelectric thin film are proposed. As one of them,

a method of crystallization of a PZT thin film called Ti seed method is proposed.

As shown in Fig. 7, the method includes forming a seed layer 9L consisting of titanium ultra thin film of about 20 nm film thickness on a surface of a lower electrode 8 consisting of platinum Pt and the like by spattering method and to form a PZT film 9P on the upper layer by sol-gel method as shown in Fig. 7. Here, mixed solution of  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$ , and  $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$  is used as a starting material, after spin-coating the mixed solution, is dried at 150°C, and temporary baking of 400°C[,] for 30 minutes is performed [at] under a dry air atmosphere. After repeating this five times, crystal growth from the ultra thin film 9L appears through crystallization annealing process of about 700°C, one minute in atmosphere of  $\text{O}_2$ .

In the method, there has been a problem that particle diameter of crystal can not be controlled because a place where crystallization starts is unstable and dispersion of characteristic is large because uniform size columnar crystal is formed so as not to obtain enough suitable characteristics, particularly at micronization micronization and high integration.

There has been a problem that the method has a place becoming titanium oxide layer ( $\text{TiO}_2$ ) or lead titanate ( $\text{PbTiO}_3$ ) layer without becoming PZT film so as to obtain good

characteristics.

There has been a problem that the method negatively affects ~~badly to~~ the substrate layer, for example, by negatively affecting such as substrate wiring because the temperature at 5 crystallization annealing was is high temperature at about 700°C.

#### Summary of the Invention

The invention is performed in view of the circumstances, 10 and an object of the invention is to provide a ferroelectric thin film that is uniform and good in crystallinity.

The invention is characterized by forming a seed layer including ultra-fine particle powder including composing element of a ferroelectric substance thin film on a surface 15 of a substrate constructing the substrate before forming the ferroelectric substance thin film and forming the ferroelectric substance thin film on an upper layer of the seed layer so as to performing crystallization making the seed layer a nucleus.

According to such the a construction, it is possible to 20 obtain a ferroelectric substance thin film that is uniform and good in crystallinity because crystallization advances well making the ultra-fine particle powder a nucleus by existence of the ultra-fine particle powder. It is desirable to make the ultra-fine particle powder from 0.5 nm to about 200 nm 25 particle diameter, particularly from 1 nm to about 50 nm particle

diameter.

Incidentally, some degree of minimum number of atoms is need needed for the ultra-fine particle powder to become a nucleus, as the ultra-fine particle powder can not become the 5 nucleus with one atom, and it is desirable to be sufficiently larger size-enough than the atomic size of about 0.1 nm. On the other hand, when the nucleus is too large, the center of the nucleus remains as Ti. Therefore, high annealing temperature is need needed for not remaining converting Ti. 10 It is impossible to form a flat and uniform ferroelectric substance thin film when the size is larger than 200 nm. There is-inconvenienee that the The nucleus is hard to scatter in solution when the nucleus is large.

Further, the concentration is desirable to be from 0.00001 15 wt% (0.1 wtppm) to about 1 wt%.

Desirably, the invention is characterized by including a process forming a seed layer including titanium ultra-fine particle powder becoming a seed and a process forming a PZT thin film on the upper layer of the seed layer.

20 According such the a construction, it is possible to obtain a PZT ferroelectric substance thin film that is uniform and good in crystallinity because crystallization advances well, thereby making the titanium ultra-fine particle powder a nucleus by the presence existenee of the titanium ultra-fine particle 25 powder of about 5 nm diameter.

Desirably, the invention is characterized by that the process forming the seed layer includes a process for applying a solution that includes including the titanium ultra-fine particle powder and a process for drying and baking.

5 According to such the a construction, it is possible to arrange the titanium ultra-fine particle powder easily and uniformly.

Desirably, the invention is characterized by that the process forming the PZT thin film includes a sputtering process.

10 Desirably, the ~~invention is characterized by that the~~ process of forming the PZT thin film further includes an annealing process for crystallization.

According to such the a construction, it is possible to easily form easily a good ferroelectric ~~substance~~ thin film 15 in crystallinity by introducing an annealing process for crystallization. ~~though~~However, it is also possible to perform crystallization at a heating process in the following forming process or to form forming an electrode with an insulating film too, because crystal growth takes place at about 450°C, which 20 is a lower temperature than that used by the related art.

The second method of the invention is characterized by including a process for applying a ferroelectric ~~substance~~ thin film applying liquid that includes including ultra-fine particle powder including comprising at least one kind of 25 composing elements of the ferroelectric ~~substance~~ thin film

on a surface of a substrate ~~constructing a substrate and a~~.

A baking process is also included.

According to such ~~the a~~ construction, crystallization from the ultra-fine particle powder advances well ~~because of~~ 5 ~~by~~ forming a thin film that includes ~~including~~ ultra-fine particle powder. Thus, [[and]] it is possible to form a thin film that is uniform and high in reliability.

Desirably, the invention is characterized by including a process for applying a PZT applying liquid that includes 10 ~~including~~ ultra-fine particle powder that becomes ~~becoming~~ a seed on a surface of a substrate ~~constructing a substrate and a.~~ A baking process is also included.

According to such ~~the a~~ construction, crystal growth starts from a seed consisting of titanium ultra-fine particle 15 powder of about 5 nm particle diameter scattered uniformly ~~in~~ ~~whole of~~ throughout the ferroelectric ~~substance~~ thin film. Therefore, it is possible to form ~~the a~~ PZT ferroelectric substance thin film that is uniform and good in crystallinity because crystallization advances well, thereby making the 20 titanium particle powder a nucleus.

Desirably, the invention is characterized by further including an annealing process for crystallization.

According to such ~~the a~~ construction, it is possible to form easily a good ferroelectric ~~substance~~ thin film in 25 crystallinity by introducing an annealing process for

crystallization. However, though it is possible to perform crystallization at a heating process in the following forming process or to form forming an electrode with an insulating film too, because crystal growth takes place at about 450°C, which 5 is a lower temperature than that used by the related art.

The third invention is characterized in that forming the ferroelectric substance film is performed by forming a seed layer including an ultra-fine particle powder. The ultra-fine particle powder includes a ~~including~~ composing element of the 10 ferroelectric substance thin film on a surface of a floating gate before forming the ferroelectric substance thin film, and by carrying out crystal ~~Crystal~~ growth making ~~makes~~ the ultra-fine particle powder a nucleus for ~~at~~ a method of manufacturing a ferroelectric substance consisting of an FET 15 of an MFMIS structure.

According to such the a construction, it is possible to obtain a ferroelectric substance thin film that is uniform and good in crystallinity because crystallization advances well, thereby making the ultra-fine particle powder a nucleus by 20 existence through the presence of the ultra-fine particle powder of about 5 nm diameter. Thus, so that it is possible to form high a ferroelectric substance memory that is high in reliability.

In the fourth invention, a forming process of the 25 ferroelectric substance film is performed by applying a

ferroelectric substance thin film applying liquid. The liquid includes including an ultra-fine particle powder including comprising at least one kind of composing elements of the ferroelectric substance thin film on a surface of a substrate 5 constructing a substrate . The and forming the ferroelectric substance thin film is formed so as to make it crystallization crystallize to produce in a method of manufacturing a ferroelectric substance memory consisting of an FET of an MFMIS structure.

10 According to such the a construction, a uniform ferroelectric substance thin film is obtained because crystal growth starts from a seed scattered uniformly in whole throughout the ferroelectric substance thin film, and it is possible to form high a ferroelectric substance memory that is high in 15 reliability at micronization micronization.

The fifth invention is characterized in that a ferroelectric substance thin film of the ferroelectric substance capacitor is formed by applying a ferroelectric substance thin film applying liquid. The liquid includes 20 including ultra-fine particle powder including comprising at least one kind of composing elements of the ferroelectric substance thin film on a surface of a first electrode. Crystallization is performed to produce and making it crystallization in a method of manufacturing a ferroelectric 25 substance memory consisting of a switching transistor and a

ferroelectric capacitor.

According to such ~~the~~ a construction, a uniform ferroelectric ~~substance~~ thin film is obtained because crystal growth starts from a seed scattered uniformly in whole throughout 5 the ferroelectric substance thin film, and it is possible to form ~~high~~ a ferroelectric ~~substance~~ memory that is high in reliability at micronization micronization.

The sixth invention is characterized in that a ferroelectric ~~substance~~ thin film of the ferroelectric 10 ~~substance~~ capacitor is formed by forming a strong seed layer including ultra-fine particle powder. The powder includes including at least one kind of composing elements of the ferroelectric ~~substance~~ thin film on a surface of a first electrode[[],]. The forming ~~the~~ ferroelectric ~~substance~~ thin 15 ~~film is formed~~ on an upper layer of the seed layer[[],]. The and forming ~~the~~ ferroelectric ~~substance~~ thin film consisting of comprises crystals being all of a size all sizes. Crystallization produces making ~~it~~ crystallization in a method of manufacturing a ferroelectric ~~substance~~ memory consisting 20 of a switching transistor and a ferroelectric capacitor.

According to such ~~the~~ a construction, it is possible to obtain a ferroelectric ~~substance~~ thin film that is uniform and good in crystallinity because crystallization advances well, thereby making the ultra-fine particle powder a nucleus and 25 to form a high ferroelectric ~~substance~~ memory high in reliability

by existence of the titanium ultra-fine particle powder of about 5 nm diameter.

Brief Description of the Drawings

5 Fig. 1 is a view showing an FRAM using an insulating film formed by a method of a first embodiment of the invention;

Figs. 2A to 2E are views showing a manufacturing process of the FRAM of Fig. 1;

10 Fig. 3 is a ~~describing~~ view depicting of the principle ~~describing~~ a method of the first embodiment of the invention;

Fig. 4 is a ~~describing~~ view showing an FRAM formed by a method of a second embodiment of the invention;

Figs. 5A to 5E are views showing a manufacturing process of the FRAM of Fig. 4;

15 Fig. 6 is a ~~describing~~ view depicting of the principle ~~describing~~ a method of the second embodiment of the invention; and

Fig. 7 is a ~~describing~~ view depicting of the principle ~~describing~~ a method of the related art.

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Detailed Description of the Preferred Embodiment

An embodiment of a ferroelectric substance memory and a method of manufacturing the same according to the invention will be described referring to the above-referenced drawings.

25 (Embodiment 1)

A ferroelectric substance memory using a ferroelectric substance capacitor using a PZT as a ferroelectric substance film will be described for in a first embodiment of the invention. A completing view of the ferroelectric substance memory is shown 5 in Fig. 1 and manufacturing process views are shown in Figs. 2A to 2E. The ferroelectric substance memory relates to a ferroelectric substance memory (FRAM) forming a ferroelectric substance capacitor on an insulating film 6 covering a surface of a substrate so as to connect one side of source-drain regions 10 2 and 3 of an MOSFET functioning as a switching transistor formed in a silicon substrate 1 and lower electrodes 8a and 8b through plugs 7[[, and crystallinity]]. Crystallinity of a ferroelectric substance thin film 9 of the ferroelectric substance capacitor is uniform. Here, symbol 5 is a gate 15 electrode formed on the surface of the substrate through a gate insulating film 4. The ferroelectric substance thin film 9 includes a crystal having a uniform particle diameter of crystal formed so as to make generate crystal growth generate from the titanium ultra-fine particle powder by previously forming a 20 seed layer, including titanium ultra-fine particle powder on a surface of the lower electrode.

That is, as shown in Fig. 1, the plugs 7 of polycrystalline silicon layer doped in high density ~~is~~ are formed, the lower electrodes 8 of two layers film of iridium 8a and iridium oxide 25 8b ~~is~~ are formed, and a ferroelectric substance thin film 9

in uniform crystallinate (See Fig. 3) is formed on the lower electrodes 8 by crystal growth making a seed layer S of titanium ultra-fine particle powder a nucleus and further forming upper electrodes 10 of two layers film of iridium oxide and iridium 5 on the upper layer of the ferroelectric substance thin film.

Next, a process for manufacturing the ferroelectric substance memory will be described with reference to Figs. 2A to 2E.

First, thermal oxidation is performed about the surface 10 of the silicon substrate 1 forming a MOSFET (not shown) in an element region formed with an element separating insulating film 1S formed by LOCOS method[, and after]. After forming the insulating film 6 of silicon oxide of about 600 nm in film thickness, a contact hole H is formed at the insulating film 15 6. After a polycrystal silicon layer is doped in high density in the contact hole so as to form the plug 7, the an iridium layer 8a of about 200 nm film thickness is formed ~~at whole~~ throughout the surface of the substrate by a spattering method and further the surface thereof is oxidized so as to become 20 iridium oxide 8b as shown in Fig. 2A.

Continuously, the iridium oxide layer is patterned to by photolithography so as to form the lower electrode 8.

After that, Ti ultra-fine particle powder of about 5 nm particle diameter is mixed with a surface active agent of 0.1 25 to 10 wt% and  $\alpha$  terpineol. The and the mixed liquid is applied

as shown in Fig. 2B.

After that, a PZT film 9P for forming the ferroelectric substance film 9 is formed as shown in Fig. 2C. Mixed solution of  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$ , and  $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$  is used as 5 a starting material. After spin coating the mixed solution, the film is dried at  $150^\circ\text{C}$ , and temporary baking of  $400^\circ\text{C}$ [[,]] for 30 minutes is performed at under a dry air atmosphere. This is repeated five times. After that, thermal treatment of about  $450^\circ\text{C}$ [[,]] for one minute under a in atmosphere of  $\text{O}_2$  is performed 10 as shown in Fig. 2D.

Thus, a ferroelectric substance film [[10]] 9 of 250 nm is formed as shown in Fig. 2E. Here, the PZT film is formed placing 0.52 for x (PZT (52/48) hereafter) in  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ .

A laminating Laminating layers of film of iridium oxide 15 and iridium ~~is~~ are formed on the ferroelectric substance film 9 by spattering. The laminating layers of film of iridium oxide layer and iridium layer form an upper electrode 10 as shown in Figure 1. Here, the iridium layer and the iridium oxide layer are formed so ~~as to be 200 nm~~ that the thickness is about 20 200 nm in all. Thus, the a ferroelectric substance capacitor is obtained.

According to such the a structure, it is possible to obtain a ferroelectric substance thin film that is uniform and good in crystallinity because crystallization advances well, 25 thereby making the ultra-fine particle powder a nucleus by

existence through the presence of the ultra-fine particle powder  
as shown in Fig. 3.

It is desirable that the ultra-fine particle powder has  
a particle diameter from 0.5 nm to about 200 nm particle diameter,  
5 particularly preferably from 1 nm to about 50 nm particle  
diameter.

Incidentally, some minimum degree of number of atoms is  
needed needed for the ultra-fine particle powder to become a  
nucleus, as the ultra-fine particle powder can not become the  
10 nucleus with one atom. [[, and it]] It is desirable that the  
nucleus to be sufficiently larger size enough than the atomic  
size of about 0.1 nm. On the other hand, when the nucleus is  
too large, the center of the nucleus remains as Ti. Therefore,  
a high annealing temperature is needed ~~need for not remaining~~  
15 converting Ti. It is impossible to form a flat and uniform  
ferroelectric ~~substance~~ thin film when the size is larger than  
200 nm. ~~There is inconvenience that the~~ The nucleus is hard  
to scatter in solution when the nucleus is large.

Further, the concentration is desirable to be from 0.00001  
20 wt% (0.1 wtppm) to about 1 wt%. Although a substance that the  
circumference of Ti ultra-fine particle powder is covered with  
is a surface active agent and organic solvent such as  $\alpha$  terpineol  
is mixed for forming the seed layer, it is also possible [[too]]  
to use xylene, toluene, 2-methoxyethanol, butanol and so on  
25 as an organic solvent.

Desirably, at the process forming the seed layer, solution including the titanium ultra-fine particle powder is applied, and after that, drying and baking are performed.

According to such the a construction, it is possible to 5 arrange the titanium ultra-fine particle powder easily and uniformly.

The process forming the PZT thin film may be by any spattering method, except sol-gel method.

Desirably, the process forming the PZT thin film further 10 includes an annealing process for crystallization.

According to such the a construction, it is possible to easily form easily a good ferroelectric substance thin film in crystallinity by introducing an annealing process for crystallization. [[, though it]] It is also possible to perform 15 crystallization at a heating process in the following forming process or to forming form an electrode with an insulating film ~~too because by~~ crystal growth at about 450°C, which is a lower temperature than the related art.

Although the ferroelectric substance memory using PZT 20 as the ferroelectric substance thin film is described for the first embodiment of the invention, it is not need to say necessary to point out that another material, such as the ferroelectric substance memory using STN as the ferroelectric substance film, may be applicable.

Next, a manufacturing process of a ferroelectric substance memory of the MFMIS structure will be described. Fig. 4 is a view showing the ferroelectric substance memory formed by the method of the invention, and Figs. 5A to 5E are views 5 of the manufacturing process.

In this example, a ferroelectric substance thin film 16 of the ferroelectric substance memory of the MFMIS structure is formed by applying sol-gel liquid including Ti ultra-fine particle powder, and after baking, by 10 crystallization-annealing so as to form the ferroelectric substance thin film 16 that is uniform and high in crystallinity.

That is, the ferroelectric substance memory is constructed by forming source-drain regions 2 and 3 formed on a surface of a silicon substrate 1, forming a floating gate 15 formed between them through a gate insulating film 4, forming a ferroelectric substance thin film 16 formed on the floating gate 15, and forming a control gate 17 formed on the ferroelectric substance thin film 16.

At During manufacturing, as shown in Fig. 5A, after the 20 surface of n-type silicon substrate 1 is oxidized thermally so as to form a silicon oxide layer 4 of about 20 nm film thickness, an iridium layer that becomes becoming the floating gate 15 is formed on the silicon oxide layer 4 using iridium as a target by a spattering method. Next, a performing thermal treatment 25 is performed at [[of]] 800°C [[,]] for one minute in under a

atmosphere of  $O_2$  so as to form an iridium oxide layer on a surface of the iridium layer.

Next, a PZT film is formed on the floating gate 15 as the ferroelectric substance film 16 by a sol-gel method as shown 5 in Fig. 5B. Titanium ultra-fine particle particles of 5 nm particle diameter and of 0.5 wt%, a surface active agent of 1 wt%, and mixed solution of  $Pb(CH_3COO)_2 \cdot 3H_2O$ ,  $Zr(t-OC_4H_9)_4$ , and  $Ti(i-OC_3H_7)_4$  are used as starting materials. After spin coating the mixed solution, the film is dried at 150°C, and temporary 10 baking of 400°C[,] for 30 minutes is performed at under a dry air atmosphere. After this is repeated five times, thermal treatment of 500°C[,] for one minute in under an atmosphere of  $O_2$  is performed as shown in Fig. 5C. Thus, a ferroelectric substance film 16 of 250 nm is formed. Here, the PZT film is 15 formed placing 0.52 for  $x$  in  $PbZr_xTi_{1-x}O_3$  (PZT(52/48), hereinafter).

Here, a uniform ferroelectric substance thin film can be obtained because crystal growth starts from the seed scattered uniformly in whole of throughout the ferroelectric substance 20 thin film so as to form high a ferroelectric substance thin film that is high in reliability at micronization micronization.

Further, an iridium layer and an iridium oxide layer are formed on the ferroelectric substance film 16 by spattering 25 so as to form a control gate 17. Here, the iridium layer and

the iridium oxide layer are formed so as to be 200 nm in thickness in all.

Then, a resist pattern R is formed on the upper layer thereof and each layer is patterned, masking the pattern as 5 shown in Fig. 5D so as to expose the surfaces of the regions that become the becoming source-drain.

After that, by injecting boron (B) ion to mask masking the gate electrode pattern, source-drain regions 2 and 3 of p-type diffusion layer are formed as shown in Fig. 5E.

10 Further, forming a layer an insulating film layer and a wiring pattern, a ferroelectric substance memory is completed.

According to such the a structure, since the ferroelectric substance film formed between the floating gate and the control gate is a film that is uniform and good in crystallinity, the 15 memory has high reliability without having dispersion of characteristics.

Although PZT is used for the ferroelectric substance film, the ferroelectric substance such as STN, SBT and the like or the high permittivity dielectric film such as BST and the like 20 are possible to apply. Material included in composing the element of the ferroelectric substance film may be applied used as the for ultra-fine particle powder.

As described above, the invention forms a seed layer including ultra grain particle particles containing an element 25 that constitutes constituting a ferroelectric substance thin

film on a surface of a substrate ~~constructing the substrate~~ before forming the ferroelectric ~~substance~~ thin film and forms the ferroelectric ~~substance~~ thin film on an upper layer of the seed layer so as to perform crystallization making the seed 5 layer a nucleus. Therefore, it is possible to obtain a ferroelectric ~~substance~~ thin film that is uniform and good in crystallinity because crystallization advances well, thereby making the ultra-fine particle powder a nucleus by existence of the ultra-fine particle powder.

10 The method of the invention includes applying applies a ferroelectric ~~substance~~ thin film applying liquid that including includes ultra-fine particle powder containing at least one kind of the elements constituting the ferroelectric substance thin film on a surface of a substrate ~~constructing~~ 15 ~~a substrate~~ and forms a thin film including ultra-fine particle powder. Therefore, crystallization advances well from the ultra-fine particle powder because of forming a thin film is formed that includes including ultra-fine particle powder that is scattered scattering in whole of throughout the thin film 20 and it is possible to form a thin film that is uniform and high in reliability.

## ABSTRACT OF THE DISCLOSURE

The invention provides a method for forming a ferroelectric substance thin film that is uniform and good in crystallinity. The method includes ferroelectric substance thin film is characterized by applying a liquid to a surface of a substrate. The liquid includes ultra-fine particle powder comprising at least one element constituting the ferroelectric thin film to a surface of a substrate. The liquid applied to the surface of substrate is then baked. forming a seed layer including ultra fine particle powder including composing element of a ferroelectric substance thin film on a surface of a substrate constructing the substrate before forming the ferroelectric substance thin film and forming the ferroelectric substance thin film on an upper layer of the seed layer so as to perform crystallization making the seed layer a nucleus.